COMPLETE POLYMER ELECTROPHORESIS MICROCHIP WITH INTEGRATED HIGH VOLTAGE AND DETECTION ELECTRODES

R.D. Henderson*, R.M. Guijt*, A. Henderson, T.W. Lewis***,**
E.F. Hilder*, P.R. Haddad* and M.C. Breadmore*
** Australian Centre for Research on Separation Science, University of Tasmania, AUSTRALIA*
***School of Engineering, University of Tasmania, AUSTRALIA*
**** School of Chemistry, University of Tasmania, AUSTRALIA*

ABSTRACT

This paper reports the first fully-integrated fully polymeric microchip for electrophoresis including electrodes for high voltage and also for contactless conductivity detection. The complete polymer microchip was demonstrated with a separation of the inorganic cations, K^+, Na^+ and Li^+ to benchmark performance. Rapid separations (30 s) with high electric field strengths (200 V/cm) yielded detection limits of 26-75 μM.

KEYWORDS: polymer, conducting polymer, integrated microchip, contactless conductivity detection

INTRODUCTION

Over the past decade there has been a strong drive towards the development of single-use 'disposable' microfluidic devices for a range of applications. While simple low-cost devices can be made in plastic due to mass replication techniques incorporation of more advanced functionality through the integration of metal electrodes attracts significant financial cost. For example, it is possible to purchase >1000 polymer chips for electrophoresis for €10 each, but a chip with the same design and external electrodes for detection costs €32.50. Moreover, microchips of the same design with integrated electrodes in direct contact with the channels for contact conductivity detection cost €125.00 each when ordering more than 30, which is 12.5 times more expensive than the simple channel-only devices.

The integration of materials such as the conducting polymer, PANI, in place of metal electrodes has the potential to reduce the costs of integration due to its low material cost and new methods of patterning such as flash lithography [1], extrusion printing [2], and laser welding [3]. Although PANI has been used previously for electrochemical sensing, only recently has PANI been shown by our group to be capable for use as a high voltage electrode [4]

EXPERIMENTAL

Polyaniline was synthesized using the rapid mixing technique as described previously [4]. Thin films of PANI were prepared by drop casting a suspension of 4 g/L de-doped PANI onto an acrylic or PDMS substrate, using 40 μL/cm2. Polyaniline films with thickness ranging from 3.6 μm for 2 layers. Prior to casting, each substrate was cleaned by soaking in 0.2 M NaOH for 5 min with mild agitation before rinsing with running MilliQ water followed by drying with lint-free paper towel. Directly before casting, the substrates were treated for 2 min with forming surface plasma (BD-20ACV, Electro Technic High Frequency Generator, USA). The films were air-dried on a level bench at room temperature for 2 hours before a second coat was applied and dried in a similar fashion. The film was then doped by dipping into 1M HCl to convert the polyaniline from the non-conducting PANI emeraldine base to the conducting emeraldine salt.

Using a simple setup in which a 50x microscope objective to focus light from a 635 nm solid-state laser onto a computer controlled XY stage, 10 μm wide non-conducting features can be welded enabling complete electrical insulation between two conducting regions of polyaniline. Patterned PANI films were covered with a layer of 17 μm dry film resist with access holes patterned in the reservoirs to make liquid contact with the PANI electrode. This was covered with a PDMS containing microchannels with a standard cross geometry and punched reservoir holes (figure 1).

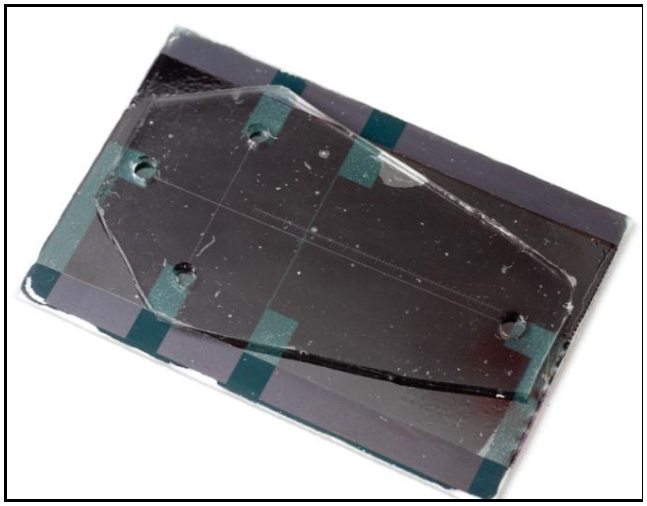

Figure 1: Photograph of a completely polymer microchip with integrated conducting polymer high voltage electrodes and detection electrodes.

Separations were performed using an in-house power supply with contactless conductivity detection using the TraceDec system (Istech, Austria). The separation electrolyte comprised 45 mM MES and 55 mM HIS with a pH of 5.9.

RESULTS AND DISCUSSION

The financial impediment regarding the development of integrated microfluidic devices with metal electrodes prompted us to consider alternative ways to integrate microelectronic pathways within microfluidic devices. Lithographically patterning of the conducting polymer, PANI, to create non-conductive regions provides a potentially low cost method for the creation of highly intricate polymer electronic circuits. We previously found that the resolution that could be achieved when patterning large areas using flash welding was low because of the nature of the light source required to fully pattern a large area. The ability to pattern PANI using finely focused light from a 635 nm laser enabled the creation of much finer features, with welded, non-conductive regions as narrow as 10 µm.

The device shown in figure 1 contains 4 high voltage electrodes, each of which were 5 mm wide and extended 12 mm from the edges of the substrate and 9 mm from the ends of the substrate The contactless conductivity detector consisted of two 200 µm wide straight electrodes with a 100 µm gap in between (figure 2). To prevent interferences, the electrodes were positioned at opposite ends of the device allowing 2 mm overlap in the sensing area. This area was used to connect the high voltage electrodes to high voltage power supply wires using alligator clips and to connect the detection electrodes to the conductivity detection electronics using copper wires and conductive glue.

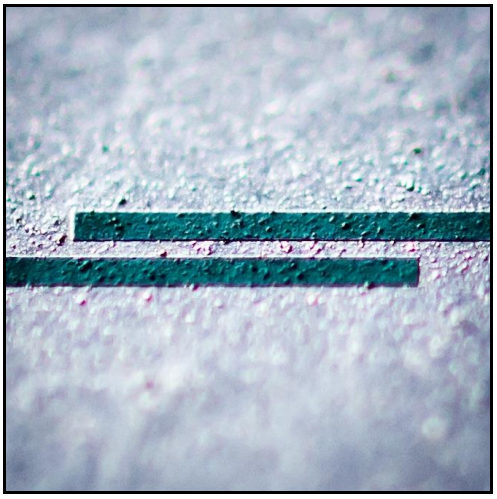

Figure 2: Photograph of the contactless conductivity detection electrodes. The electrodes are 200 µm wide separated by a gap of 100 µm.

The functionality of the fully-integrated fully-polymer microchip was tested with the electrophoretic separation of a mixture of Li^+, Na^+ and K^+ in 45 mM MES / 55 mM HIS BGE with a pH of 5.9. Separations were performed in a standard cross microchannel using pinching and pullback techniques that are well described within the field. Voltages of up to 300 V were applied on the PANI electrodes, but it is important to note that the application of the voltages was not limited by the PANI, but by the risk of destruction of the detection electronics following dielectric breakdown of the 17 um thin insulating film. A representative separation achieved under these conditions is shown in figure 3. The separation of this mixture of ions under these conditions was selected to allow the system to be benchmarked against existing published separations using contactless conductivity detection.

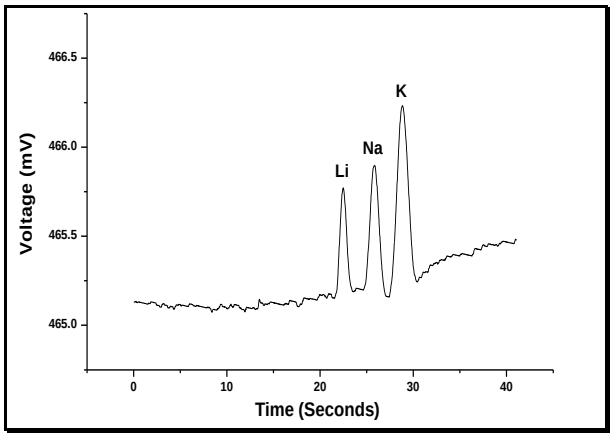

Figure 3: Electropherogram of alkali metals in a completely integrated polymer microchip with polymer high voltage and detection electrodes.

The limits of detection (LOD) as calculated at 3x noise for each of the alkali metals used during this separation were Li^+ 72.7 µM (0.50 ppm), Na^+, 29.3 µM (0.67 ppm) and K^+, 26.2 µM (1.02 ppm). This is comparable to most LODs of around 30 to 100 µM being reported with integrated contactless conductivity detection [5].

ACKNOWLEDGEMENTS

This research was supported by the Department of Education, Science and Technology (DEST) Special China Fund CH060008 and a University of Tasmania Cross Theme Grant. The authors would also like to acknowledge the Australian Research Council for a QEII fellowship (DP0984745) awarded to Michael Breadmore, a Future Fellowship (FT0990521) awarded to Emily Hilder, and a Federation Fellowship (FF0668673) awarded to Paul Haddad.

REFERENCES

[1] J. Huang and R.B. Kaner, "Flash welding of conducting polymer nanofibres", *Nature Materials*, issue 3, pp 783-786, 2004.

[2] C.A. Mire, A. Agrawal, G.G. Wallace, P. Calvert, M. het Panhuis, "Inkjet and extrusion printing of conducting poly(3,4-ethylenedioxythiophene) tracks on and embedded in biopolymer materials", *J. Mater. Chem.*, issue 21 pp 2671-2678, 2011.

[3] R.D. Henderson, O.S. Hutter, R.M. Guijt, T.W. Lewis, E.F. Hilder, P.R. Haddad, M.C. Breadmore, Laser welded polyaniline circuits, Proc. Micro Total Analysis Systems 2010, Kluwer Academic Publisher, Dordrecht, The Netherlands, 1232-1233.

[4] R.D. Henderson, R.M. Guijt, P.R.. Haddad, E.F. Hilder, T.W. Lewis, and M.C. Breadmore, "Manufacturing and application of a fully polymeric electrophoresis chip with integrated polyaniline electrodes.", *Lab-on-a-chip*, issue 10, pp 1869 – 1872, 2010.

[5] P. Kubáň, and P.C. Hauser, "Capacitively coupled contactless conductivity detection for microseparation techniques - recent developments", *Electrophoresis*, vol. 32, issue 1, pp 30-42, 2011.

CONTACT

*M.C. Breadmore, tel: +61-3-62262154; mcb@utas.edu.au